

# Layered heat resistant (Nb–V) composites with intermetallic hardening, obtained by diffusion welding

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**Abstract:** *The microstructure and characteristics of the heat resistance of layered composites of Nb–V alloys and intermetallic compounds with aluminum are presented. The composites obtained by diffusion welding under pressure of packages of aluminum foils and foils of niobium alloys with 5, 10, and 15 at. % vanadium had structures representing an alternation of viscous-plastic layers and reinforcing layers of aluminides. The composites were characterized by a viscous-plastic nature of fracture and higher values of strength at room temperature and temperatures up to 1300°C, in comparison with composites without vanadium.*

**KEYWORDS:** LAYERED COMPOSITE, NIOBIUM-VANADIUM ALLOY, INTERMETALLIC COMPOUND, HEAT RESISTANCE, DIFFUSION WELDING, REACTIVE DIFFUSION, MULTILAYER STRUCTURE, STRENGTH, CREEP

## 1. Introduction

There is an objective need for the development of new-generation structural heat-resistant materials. Niobium alloys are one of the few major contenders for this role. Interest in alloys lies in the production of machine parts and mechanisms from them for operation in a loaded state at temperatures up to 1300°C and, possibly, higher. The requirements for materials are high values of strength, creep resistance, and phase stability at operating temperatures in combination with good crack resistance at room temperature and low density [1, 2].

At present, nickel superalloys remain the most common material for manufacturing, for example, turbine blades. However, their operational properties came very close to the theoretical limit and their further increase became objectively impossible [3, 4]. Instead of Ni alloys, alloys based on the systems Nb–Si, Nb–Al, Mo–Si and some others are being investigated [5–10]. At this point it is necessary to explain that the mentioned works refer to cast alloys. But they do not in the least reflect the real scale of published works devoted to high-temperature alloys obtained by various melting technologies. The heat-resistant composite considered in this communication is formed using a technology that has no analogs with melt methods.

The combination of Nb-alloy and its compounds with Al, Si and C in the structure of the composite reduces its density in comparison with the density of niobium and its alloys, due to the relatively low density of aluminides [8]. But, since all intermetallics are brittle, especially under normal conditions, the problem of crack resistance of the material arises, which, however, is not insurmountable. The optimal organization of the composite structure is capable of providing it with acceptable fracture toughness at room temperature.

For the formation of a layered structure of heat-resistant materials based on the Nb–Al system, the methods of layer-by-layer spraying are widely used in world practice [11–14]. In Russia, for materials with layered structures, the solid-phase technology is more accepted, which consists in diffusion welding of artificially formed multilayer packages or in diffusion welding and subsequent rolling of packages, in particular, on a vacuum rolling mill and then rolling at room temperature [15, 16]. In such a method, the satisfactory crack resistance required by laminated composites is achieved by alternating brittle layers of intermetallic compounds with relatively plastic layers of base metal solid solutions. If we bear in mind the scale of technologies for producing a composite in the future, then we believe that spray technologies are inferior to technologies of diffusion welding and rolling.

In this work, we use melting methods only to obtain niobium-vanadium alloys.

Despite a fairly large number of works on high-temperature materials of a new generation, there are no data in the literature on the effect of various metals, in particular, vanadium, on the structure and mechanical characteristics of layered Nb composites. According to the data of a fairly large number of works on the effect of vanadium on the mechanical properties of cast alloys, alloying with vanadium leads to an improvement in their ductility. Similar studies have been undertaken in this work.

## 2. Materials, diffusion welding of bags and research methods

Nb- and V-rolled products were used as starting metals, from which niobium alloys with 5, 10, and 15 at. % Vanadium were smelted by the method of levitation at argon pressure  $(0.35–0.45) \times 10^5$  Pa in a suspended state with a rotating frequency electromagnetic field ~200 kHz. After holding in the liquid state for 1–2 min, the field was turned off, and the samples fell under the action of gravity into a Cu mold weighing 480 g with an inner “flat cavity” 4 mm thick and 20 mm long, where the ingot crystallized under quenching conditions. The resulting ingots in the form of plates with a thickness of 4 mm were inserted into stainless steel capsules for protection against possible oxidation and rolled on a vacuum rolling mill with preheating to 1000°C and a degree of deformation of ~50%. After hot rolling, the samples were removed from the capsules and rolled at room temperature to a strip 150 μm thick.

Multilayer packages were assembled from alternating foils of rolled Nb–V ingots and Al foils 12 μm thick, laid in two layers. The calculated thickness of the package was ~2 mm. The formation of the layered structure of the composites was carried out in the process of diffusion welding (DW) of multilayer packets, which was carried out on a unit with a graphite heater, designed for a maximum load of 10 T and a temperature of up to 1700°C. The package to be welded was placed between the movable and fixed punches. Two layers of Graflex graphite tape were laid between the outer surfaces of the package and the punches. The welding temperature was controlled by a (W–Re) thermocouple.

The packages were welded in a vacuum of at least  $10^{-4}$  Torr, first at 500°C for 1 h and a pressure of 4.1 MPa. Then the temperature was increased to 1700°C, and the bag was kept for 15 minutes without pressure, and then for another 15 minutes under a pressure of 30.6 MPa. After welding, the packages had dimensions  $35 \times 20 \times 2$  mm.

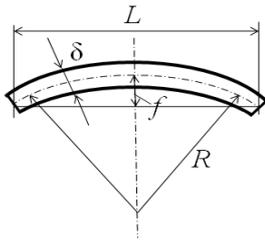
The resulting laminated composites were cut into rods for structural studies and mechanical tests for three-point bending and fracture toughness. After cutting, all surfaces of the samples were first subjected to abrasive grinding and then polishing.

Microstructure studies and local X-ray spectral analysis (LXSA) were carried out on digital scanning electron microscopes Tescan VEGA-II XMU and CamScan MV230 at an accelerating voltage of 20 kV and an electron probe current of 200 pA. Размер зонда – 0,16 мкм. The characteristic X-ray spectra were processed using a software package developed by Oxford Instruments, the calculation part of which is based on the PAP matrix correction algorithm [17].

Test samples of the short, with a loading rate of 0.5 mm/min, and long durability was carried out at temperatures of from 20 to 1300°C according to the scheme 3-point bending in the vacuum chamber, combined with the test machine «Instron», a high purity argon. To ensure the proper rigidity of the tooling during temperature tests, the supports were made of special heat-resistant ceramics based on silicides of refractory metals.

Ultimate strength [18]  $\sigma_B$  was determined at maximum load  $P$  according to the well-known formula:  $\sigma_B = 3PL/2bh^2$ , where  $P$  – load,  $L$  – distance between supports,  $b$  and  $h$  – width and height of the sample, respectively.

The creep of the composites was investigated on samples with dimensions  $2.5 \times 2 \times 20$  mm at  $1300^\circ\text{C}$  in an argon atmosphere.



Determination of the relative strain rate  $\dot{\epsilon}$  in the section of steady-state creep was carried out on the basis of the problem of rod bending (Figure 1).

**Figure 1.** Rod with thickness  $\delta$  in bending:  $f$  – deflection,  $R$  – bending radius

According to this task  $f = R - \sqrt{R^2 - \frac{L^2}{4}}$  (1), where  $L$  is the distance between the supports. For the case when  $R \gg L$ :  $f = R - R(1 - \frac{1}{8} \frac{L^2}{R^2})$  (2), where  $R = \frac{1}{8} \frac{L^2}{f}$ . Then the relative deformation  $\epsilon$  is equal to:  $\epsilon = \frac{2\pi(R + \frac{\delta}{2}) - 2\pi R}{2\pi R} = \frac{\delta}{2R}$  (3)

With the same designs of the initial packages and modes of DS, the macro- and microstructures of the composites (Nb5V) / Al and (Nb15V) / Al differed significantly (Fig. 4.). Substituting the expression for  $R$  in (3), we obtain  $\epsilon = \frac{\delta}{2} \frac{1}{\frac{1}{8} \frac{L^2}{f}} = \frac{4\delta}{L^2} f$  and  $\dot{\epsilon} = \frac{\partial \epsilon}{\partial t} = \frac{4\delta}{L^2} \frac{\partial f}{\partial t} = \frac{4\delta}{L^2} \dot{f}$  (4).

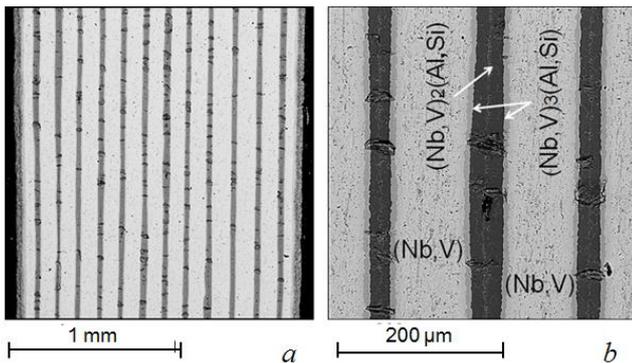
We used the following form of the dependence of the creep rate on stress and temperature:  $\dot{\epsilon} = \frac{4\delta}{L^2} \dot{f}$  (5), where  $\dot{\epsilon}$  – strain rate ( $\text{s}^{-1}$ ),  $\dot{f}$  – deflection rate ( $\text{mm/s}$ ),  $\delta$  – specimen height (mm) and  $L$  – distance between supports (mm).

### 3. Experimental results

#### 3.1. Microstructure of composites

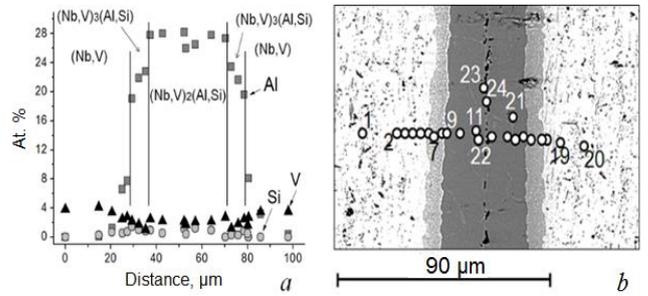
The melted and rolled Nb–V alloys had a homogeneous structure of continuous solid solutions of Nb and V without any other structural components.

The cross-sectional structure of the composite with the Nb–5 at. % V (Fig. 2, a) was an alternation of light layers up to  $100 \mu\text{m}$  thick and thin (about  $10 \mu\text{m}$ ) dark layers. At higher magnification, they had three layers (Fig. 2, b)



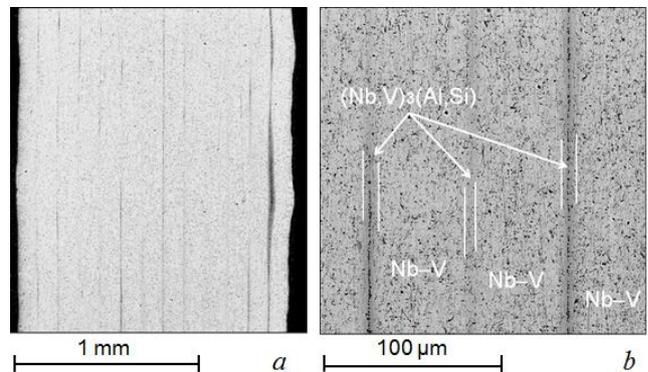
**Figure 2.** Macro- (a) and microstructure (b) of the layered composite Nb5V/Al based on the alloy Nb–5 at. %V after DW

According to local X-ray diffraction data (Fig. 3, a), the structure of diffusion layers in the (Nb5V)/Al composite consisted of a  $(\text{Nb},\text{V})_2(\text{Al},\text{Si})$  compound layer  $30\text{--}35 \mu\text{m}$  thick enclosed between two thin ( $5\text{--}8 \mu\text{m}$ ) by layers of the compound  $(\text{Nb},\text{V})_3(\text{Al},\text{Si})$ . In both intermetallic compounds, silicon was found at a level of 0.5 at. %, which was present in aluminum as an impurity. Regarding the distribution of vanadium, we can say that its presence in niobium is limited to 4 at. %, and in layers of intermetallic compounds  $(\text{Nb},\text{V})_3(\text{Al},\text{Si})$  and  $(\text{Nb},\text{V})_2(\text{Al},\text{Si})$  – 0.5 and 1 at.%, respectively.



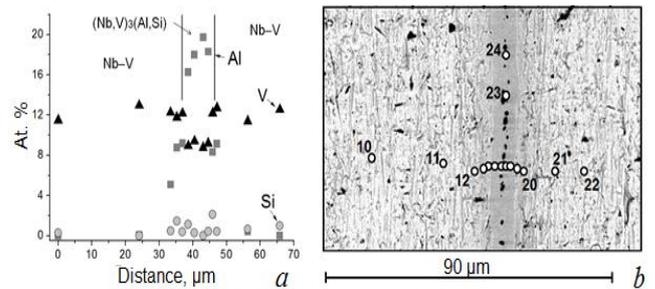
**Figure 3.** Results of local XS-analysis (a) and microstructure of the interaction zone between the layers of alloy and aluminum (b) in the layered composite Nb5V/Al after diffusion welding: 1–24 – points local XSA

The microstructure of the layer formed as a result of the mutual diffusion of aluminum and the alloy is shown in Fig. 3, b. Note the presence in the central part of the  $(\text{Nb},\text{V})_2(\text{Al},\text{Si})$  compound layer of a line of dark inclusions of  $\text{Al}_2\text{O}_3$  oxide (23 and 24 – points of local XSA).



**Figure 4.** Macro- (a) and microstructure (b) of a layered composite Nb15V/Al based on an alloy Nb–15 at. %V after DW

Similar studies are presented for a composite based on an Nb – 15 at. % V. With the same designs of the initial packages and modes of DW, the macro- and microstructures of the composites (Nb5V)/Al and (Nb15V)/Al differed significantly (Fig. 4).



**Figure 5.** Results of local XS-analysis (a) and microstructure of the interaction zone between the layers of the alloy and aluminum (b) in the layered Nb15V/Al composite after diffusion welding: 1–24 – points of local XSA

The layered structure of the composite with 15 at. % vanadium is characterized by "diffuseness" of the macro- and microstructure with an almost complete absence of interlayer boundaries (Fig. 4, b). In addition, it can be noted that the "saturation" of the niobium-vanadium alloy layers with ultradispersed inclusions is significantly higher than in the composite with 5 at. % V (compare Figs. 2, b and 4, b). This is most likely due to the presence of finely dispersed carbide inclusions formed during the welding of packets due to the presence of CO in the atmosphere of a chamber with a graphite heater. Confirmation of this can be obtained when compared to composites microstructure layers of Nb-V alloys at high magnification (cp. Fig. 3, b and 5, b). It is clear that the Nb15V/Al composite contains a significantly larger amount of light gray needle-like inclusions than the Nb5V/Al composite.

The results of the LXS-analysis of the composite with 15 at. % vanadium, shown in Fig. 5, a showed that the layer formed during diffusion welding is a compound  $(\text{Nb},\text{V})_3(\text{Al},\text{Si})$ , in which 8 at% vanadium is dissolved. Vanadium is present in the layers of the (Nb-V)-alloy in an amount of 12 at. %. Local analysis points 23 and 24 (see Fig. 5, b) show  $\text{Al}_2\text{O}_3$  inclusions in the center of the  $(\text{Nb},\text{V})_3(\text{Al},\text{Si})$ -layers.

Summarizing the results of microstructural studies, it can be noted that:

- the layered structure of the composites consisted of viscous-plastic layers of (Nb-V)-alloys and strengthening intermetallic layers of  $(\text{Nb},\text{V})_3\text{Al}$  and  $(\text{Nb},\text{V})_2\text{Al}$  compounds with a low silicon content;
- the solubility of vanadium in the layers of the intermetallic compound  $(\text{Nb},\text{V})_3(\text{Al},\text{Si})$  was  $\sim 0.5$  in the Nb5V/Al composite, from 3 to 4 – in the Nb10V/Al composite, and 8 at. % – in the Nb15V/Al composite;
- the vanadium concentrations in the layers of the intermetallic compound  $(\text{Nb},\text{V})_2(\text{Al},\text{Si})$  were at the level of  $\sim 1$  and  $\sim 5$  at% for the composites Nb5V/Al and Nb10V/Al, respectively.

In addition, in the diffusion zones of composites with alloys Nb-5 and 10 at. % V, a full set of intermetallic compounds of the Nb-Al system could be observed, such as:  $(\text{Nb},\text{V})_3(\text{Al},\text{Si})$ ,  $(\text{Nb},\text{V})_2(\text{Al},\text{Si})$  and  $(\text{Nb},\text{V})(\text{Al},\text{Si})_3$ . However, the Nb15V/Al composite contained only the compound  $(\text{Nb},\text{V})_3(\text{Al},\text{Si})$ , which in places transforms into a "concentrated" solid solution of aluminum in the Nb-15 at. % V alloy. Hence it follows that vanadium accelerates the formation of intermetallic compounds of niobium with aluminum.

### 3.2. Flexural strength tests

The dependence of the short-term bending strength  $\sigma_B$  of the composites on the test temperature in the range from room temperature to 1300°C is shown in Fig. 6. The strength of the composites, depending on the vanadium content in the Nb-V alloy, showed a monotonic increase from 660 to  $\sim 1215$  MPa both at room temperature and at 1300°C – from  $\sim 265$  to 390 MPa.

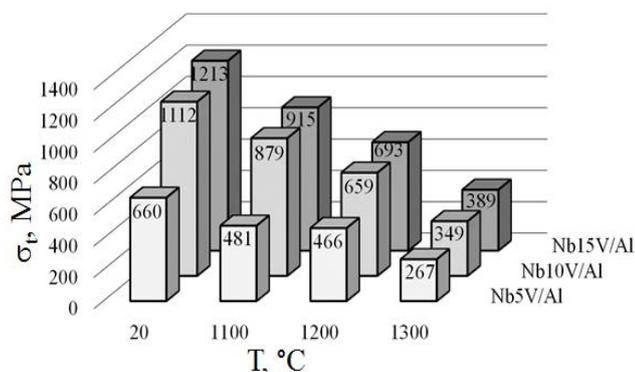
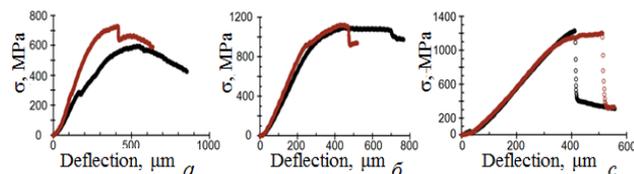


Figure 6. Dependence of the average values of  $\sigma_v$  on the test temperature and vanadium content

Bending tests of composite specimens at room temperature showed a ductile fracture pattern (Fig. 7). The load was applied perpendicular to the layers. The maximum on the load-displacement

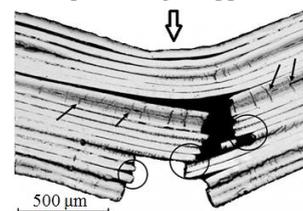


curves corresponded to a deflection without fracture equal to 400  $\mu\text{m}$ . Almost all composite samples of alloys Nb-5 and 10 at. % V continued to bend without destruction, up to a deflection of 700–800  $\mu\text{m}$ .

Figure 7. Typical test curves for laminated composites at room temperature: a – Nb5V/Al, b – Nb10V/Al, c – Nb15V/Al

If the composite had some kind of destruction (see Fig. 7, c), then it was characterized by a "layered" mechanism. Delamination was observed along the brittle intermetallic components of the sample, as less crack-resistant structural elements in the composite (Fig. 8). The arrows also show short transverse cracks in the intermetallic layers. On the contrary, when individual layers of the (Nb-V)-alloy were destroyed, viscous-plastic signs appeared. All the ends of the layers had a thinning of their middle part testifying to this.

Figure 8. The nature of the destruction of the investigated layered composites Nb15V/Al at room temperature



### 3.3. Creep tests

The experimental dependences for composite specimens that were tested for creep at 1300°C are shown in Fig. 9 and are summarized in table. 1. The so-called 100-hour strength or the magnitude of the stress causing deformation in the composite equal to 1% per 100 hours was estimated.

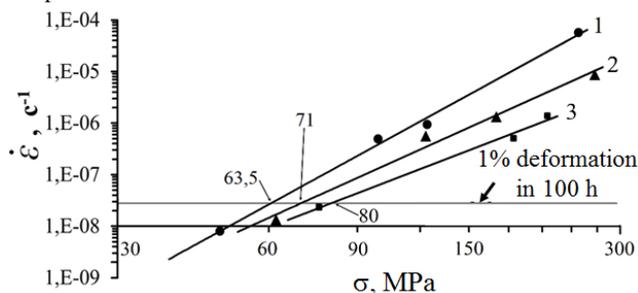


Figure 9. Dependences of the creep strain rate on stress for composites Nb5V/Al (1), Nb10V/Al (2) and Nb15V/Al (3) at a temperature of 1300°C

Tests of composites for creep at 1300°C showed the following results: the magnitude of the stress causing deformation in the composite equal to 1% per 100 h or the so-called 100-hour strength of composites based on niobium alloys with 15, 10, and 5 at. % V was equal to 80, 71 and 63.5 MPa.

Table 1. Results of creep tests of composites

| Композит | 100-часовая прочность $\sigma_{100}$ , МПа | Показатель степени, n |
|----------|--|-----------------------|
| Nb5V/Al  | 63,5                                       | 3,75                  |
| Nb10V/Al | 71,0                                       | 4,40                  |
| Nb15V/Al | 80,0                                       | 5,73                  |

However, the exponents n (from 3.75 to 5.73) of the composites are rather large, which indicates the sensitivity of the composites under study to a change in the applied voltage and can negatively affect the operational properties of the material.

### 3.4. Discussion of the results obtained

Microstructure studies showed that vanadium accelerated reactive diffusion between layers of Nb-V and Al alloys in welded NbV/Al packages. This followed from the fact that under the same

welding conditions in a composite with an Nb–5 at. %V, the interaction zone consisted of  $(\text{Nb},\text{V})_2(\text{Al},\text{Si})$  and  $(\text{Nb},\text{V})_3(\text{Al},\text{Si})$  layers bounded by explicit phase boundaries. In contrast, in a composite with 15 at. %V, the interaction zone was characterized by an almost complete absence of phase boundaries and consisted only of the compound  $(\text{Nb},\text{V})_3(\text{Al},\text{Si})$ . The composite of Nb-alloy with 10 at. %V occupied an intermediate position. Compared to other composites, the best strength properties were for the Nb15V/Al composite.

The different solubilities of vanadium in the intermetallic compounds  $\text{Nb}_3\text{Al}$  and  $\text{Nb}_2\text{Al}$  can be explained by referring to the phase diagrams of Nb–Al and V–Al. At atmospheric pressure, the V–Al phase diagram does not contain the  $\text{V}_3\text{Al}$  compound, which is related to the  $\text{Nb}_3\text{Al}$  compound. But on the other hand, it contains a "twin" compound of the  $\text{Nb}_2\text{Al}$  intermetallic compound (33.3 at. % Al) –  $\text{V}_3\text{Al}_3$  (37.5 at. % Al). Hence, the higher solubility of vanadium in the intermetallic compound  $\text{Nb}_2\text{Al}$  than in  $\text{Nb}_3\text{Al}$ .

The achieved results in terms of strength are comparable with similar data for highly alloyed eutectic alloys of the Nb–Si system [19], but in terms of viscos-plastic properties they are much superior. But the fact is that if the fracture toughness of the composites obtained is calculated according to the generally accepted method after bending tests of notched specimens, then, due to their high plasticity, its calculations will be incorrect. Therefore, we have no numerical values for this characteristic of composites. By the method we used, we tested materials with fracture toughness of  $25 \text{ MPa}\cdot\text{m}^{1/2}$  and even more. Such values were considered very high. Returning to niobium-vanadium alloys, one can foresee that their fracture toughness values can exceed  $25\text{--}30 \text{ MPa}\cdot\text{m}^{1/2}$ .

#### 4. Conclusions

1. From the data of local X-ray spectral analysis, it followed that vanadium in the intermetallic layers  $\text{Nb}_3\text{Al}$  and  $\text{Nb}_2\text{Al}$  was dissolved in significantly different amounts, respectively:

– 0.5 and 1.0 – in the Nb5V/Al composite with its content in the alloy equal to 4 at. %;

– 3.5 and 5.0 – in the Nb10V/Al composite with its content in the alloy equal to 8 at. %.

2. Mechanical tests of laminated composites for short-term strength showed a monotonic increase in strength with an increase in vanadium content in the Nb–V alloy, both at room temperature and at  $1100\text{--}1300^\circ\text{C}$ . Mechanical tests of laminated composites for short-term strength showed a monotonic increase in strength with an increase in vanadium content in the Nb–V alloy, both at room temperature and at  $1100\text{--}1300^\circ\text{C}$ .

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